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(54) ANTIPERSPIRANTS

(71) We, UNILEVER LIMITED, a British company, of Unilever House, Blackfriars, London EC4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

5 This invention relates to materials having antiperspirant activity, more especially to processes for their production. 5

For inhibiting perspiration, the application to the skin of many different antiperspirant active compounds has been described in the literature. However, those compounds most widely used in commercial products at the present time are basic aluminium halides, especially aluminium chlorhydrate, which has an Al/Cl molar ratio of about 2. These active compounds are applied to the skin from a variety of applicator types including aerosol sprays, pump sprays, squeeze packs, roll-ons and stick applicators. Thus aluminium chlorhydrate, for example, is employed as the active ingredient of various liquid, cream, stick or dry powder antiperspirant compositions. However, in spite of the popularity of aluminium chlorhydrate the presently available products are capable of producing only limited reduction in perspiration. 15

In Specification No. 1 568 831 (copending application No. 1401/76) there is described an improved antiperspirant active compound which comprises a basic aluminium chloride, bromide, iodide and nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound forms in water a solution containing polymeric species of a size greater than 100 Angstroms within which species there is contained at least 2% by weight of the total aluminium. Since in aqueous solutions of the basic aluminium compounds the halide or nitrate is in ionic form the polymeric species present are hydroxy-aluminium species. The antiperspirant active compound may be employed in the form of an aqueous solution or the solution may be spray dried to give a hydrated compound of the empirical formula 25

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$$\text{Al}_2(\text{OH})_{6-a}\text{X}_a \cdot n\text{H}_2\text{O}$$
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where X is Cl, Br, I or NO_3
 a is from about 0.3 to 1.5
 n is from about 0.5 to 8.

35 As described in said copending application these special forms of basic aluminium compounds which in aqueous solution contain polymeric species having a size greater than 100 Angstroms within which at least 2% by weight of the total aluminium is contained, may be prepared by heating aqueous solutions of basic aluminium compounds at elevated temperature. The production of the desired species depends on the appropriate choice of the reaction conditions which are interrelated. It is preferred to use temperatures of from 80°C to 140°C. The period of heating may be shorter as higher temperatures are used, ranging for example from 0.5 hour to 30 days. Of importance is the concentration of the basic aluminium compound starting material. The rate of production of the higher polymeric species of the basic aluminium compound decreases as the concentration of the 45

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solution is increased and at the above temperatures the concentration should be no more than about 35% by weight.

The present invention in one aspect relates to an improvement in the above-described process.

5 We have discovered that the presence of an amino acid, preferably glycine, in the aqueous solution of the basic aluminium compound increases the rate at which the species having a size above 100 Angstroms are formed. By including an amino acid in the reaction mixture either at the commencement or during the reaction one can produce the desired polymeric species from starting solutions of higher concentration and/or produce a given amount of the polymeric species in a shorter time and/or at a lower temperature. 10

The process of the present invention comprises heating an aqueous solution of a mixture of a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of 6.5 to 1.3:1 and an amino acid, the concentration of the basic aluminium compound in such solution and the temperature and time of heating 15 the solution being such that there is produced in the solution polymeric species having a size greater than 100 Angstroms, said species being produced in such amount that 2 to 80% by weight of the total aluminium is contained within such species. 15

The amino acid, which preferably contains 2 to 10 carbon atoms, may be a neutral amino acid by which is meant an amino acid containing an equal number of unneutralised amino and acidic groups. Examples of neutral amino acids are glycine, alanine, phenylalanine, 20 valine, sarcosine, leucine and lysine hydrochloride. However, other amino acids may be used, for example arginine, ornithine and lysine which are basic amino acids, that it amino acids which contain more unneutralised amino than acidic groups. 20

The amount of the amino acid is preferably such that the aluminium to amino acid molar ratio is from 20:1 to 1:1. 25

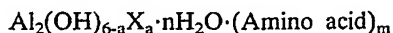
The basic aluminium compound in the solution subjected to the heat treatment preferably has an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 4 to 1.3:1, more particularly 2.5 to 1.6:1.

The weight of the aluminium in the species having an effective diameter above 100 30 Angstroms is preferably 5 to 60%. 30

The production of the desired species depends on the appropriate choice of the reaction conditions which are interrelated. It is preferred to use temperatures of from 80°C to 140°C. The period of heating may be shorter as higher temperatures are used, ranging for example from 0.5 hour to 30 days. Of importance is the concentration of the basic aluminium compound. As higher concentrations are used (other conditions being constant) the rate of 35 production of the species having an effective diameter greater than 100 Angstroms decreases. However, by the inclusion of an amino acid in the reaction mixture in accordance with the invention, the rate of reaction, for a given temperature, is increased. Thus in the process of the invention higher concentrations can be used to obtain a given amount of the desired polymeric species in a given time. In particular, substantial amounts 40 of the polymeric species have been obtained at 120°C from solutions of aluminium chlorhydrate of a concentration of 40% and even higher concentrations. The concentration of the solution of the basic aluminium compound will usually be at least 5%. Under appropriate conditions, solutions of concentration up to 60% can be used. 45

The conditions of heat treatment described above have been found to give rise to the improved basic aluminium compound in amorphous form, and in particular the formation of boehmite, as determined by X-ray diffraction, has not been observed. The production of a substantial amount of boehmite or other crystalline forms of alumina would be considered to be disadvantageous. 50

The aqueous solution of the more active antiperspirant compound comprising the higher polymeric species as defined, and produced by the process of the invention, may, if desired, be evaporated to concentrate the solution or it may be dried to give a solid hydrated material. As with untreated aluminium chlorhydrate, for example, drying conditions which lead to both the loss of water of condensation and hydrochloric acid should be avoided as 55 these may lead to irreversible degradation of the treated basic aluminium compound. Any suitable method of drying may be used, spray drying being a particularly useful method. The spray drying method described in US Patent No. 3,887,692 may be employed. The solid material may be ground or milled as required, more particularly to a particle size below 100 microns such that the particulate compound is suitable for use in an aerosol 60 powder spray product. Drying should be effected in such manner as to give a product having a water content consistent with the following empirical formula 60



where X is Cl, Br, I or NO₃, *a* is from 0.3 to 1.5, *n* is from 0.5 to 8, preferably 0.5 to 4, and *m* indicates the amount of amino acid added and is preferably 0.1 to 2.

The antiperspirant agent produced by the process of the invention may be employed directly as an antiperspirant composition in the form of the solution, or it may be used in antiperspirant compositions in the form of a powder obtained from such solution, or again as a solution obtained from such powder. Various examples of suitable antiperspirant compositions are described in the copending application referred to above.

Thus in accordance with one aspect of the invention there is provided an antiperspirant composition comprising an aqueous solution of an antiperspirant active material produced by the process of the invention in combination with an adjunct which is a perfume, thickener, alcohol or propellant. The anti-perspirant composition may be in the form of a lotion comprising an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight and 0.1 to 5% by weight of a thickening agent. Suitable thickening agents for antiperspirant lotions are well known to those skilled in the art, and include for example, magnesium aluminium silicates. Thickening may also be effected by emulsifying an oil or the like in the composition. Furthermore, the composition may comprise an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight, the amino acid and from 0.1 to 2% by weight of perfume.

The composition may comprise an aqueous alcoholic solution of the basic aluminium compound and amino acid containing from up to 75% by weight of a C₁-C₃ aliphatic alcohol. These aqueous alcoholic compositions preferably contain ethanol, propanol, isopropanol or a mixture thereof as the alcohol. Antiperspirant compositions comprising an aqueous solution of the basic aluminium compound and the amino acid may contain from 1 to 80% by weight of a propellant.

The antiperspirant composition may also comprise in combination a powdered antiperspirant active material obtained by drying a solution obtained by the process of the invention and a powdered inert solid diluent or organic liquid carrier. The composition may be in the form of a powder aerosol composition comprising a suspension of the basic aluminium compound/amino acid complex in particulate form in a liquid carrier, said composition also comprising a propellant. In particular the composition may be in the form of a powder aerosol composition comprising

- A. from about 1% to about 12% by weight of said basic aluminium compound/amino acid complex in powder form;
- B. from about 0.1% to about 5% by weight of a suspending agent;
- C. from about 1% to about 15% by weight of a carrier liquid; and
- D. from about 70% to about 96% by weight of a propellant.

The carrier liquid may for example be a non-volatile non-hygroscopic liquid as suggested in US Patent No. 3,968,203. Especially useful are carrier liquids which have emollient properties and a number of these are referred to in British Patent Specification No. 1,393,860. Especially preferred are fatty acid esters such as isopropyl myristate and those esters referred to in British Patent Specification No. 1,353,914 such as dibutyl phthalate and diisopropyl adipate.

Various other carrier liquids for powder suspension aerosols are suggested in US Patent Specifications Nos. 3,833,721, 3,833,720, 3,920,807, 3,949,066 and 3,974,270 and in British Patent Specifications Nos. 1,341,748, 1,300,260, 1,369,872 and 1,411,547. Volatile carrier liquids may also be used such as ethanol or a volatile silicone as described in South African and British Patent Specifications Nos. 75/3576 and 1,467,676, respectively.

The ratio of total solids in the compositions to the carrier liquid may vary over a wide range, for example from 0.1 to 3 parts of the powder per part by weight of the carrier liquid.

The propellant can be a liquefied hydrocarbon, halogenated hydrocarbon or a mixture thereof. Examples of materials that are suitable for use as propellants are given in the above-mentioned patents and include trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, propane, butane, 1,1-difluoroethane, 1,1-difluoro-1-chloroethane, dichloromono-fluoromethane, methylene chloride, isopentane and isobutane, used singly or admixed. Trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, and isobutane, used singly or admixed, are preferred.

Examples of materials that are suitable for use as permanent gas propellants are nitrogen, carbon dioxide and nitrous oxide.

It is common practice to include in aerosol powder spray compositions a material to assist in the suspending of the powder in the liquid vehicle. The materials prevent compacting of the powder and they may also act as thickening or gelling agents for the liquid vehicle. Especially preferred are hydrophobic clays and colloidal silicas. Hydrophobic clays are available under the trade mark "Bentone", eg Bentone 34 or Bentone 38, and their use as

suspending agents are described in a number of patent specifications including US Patent Specification No. 3,773,683. Suitable colloidal silicas include Aerosil 200 and Cab-O-Sil M-5 as well as other grades; "Aerosil" and "Cab-O-Sil" are trade marks.

5 The antiperspirant composition may simply comprise from 5 to 40% by weight of the amino acid-containing aluminium compound in powder form, the remainder consisting essentially of an inert powder material, such a talc or starch, for example. 5

The invention also relates to packages consisting of the combination of an antiperspirant composition comprising an antiperspirant active agent produced by the process of the invention and an applicator for applying the antiperspirant composition to the skin. The package may be one in which the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises a suspension of said antiperspirant active agent in particulate form in a liquid carrier which may be in admixture with a propellant. Furthermore, the package may be one wherein the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of said antiperspirant active agent. In this case the aqueous solution may be discharged by a propellant gas or by a finger-operated pump mechanism or by containing the composition within a container of pliable material whereby by squeezing the container the composition is expelled through the spray valve. Another form of package is one in which the applicator is a roll-on applicator and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of the said antiperspirant active agent. Furthermore, the package may be one wherein the applicator is an applicator for dispensing a powdered material and the antiperspirant composition is a powdered composition including said antiperspirant active agent in powder form. The applicator may also be a stick applicator for holding an antiperspirant composition in the form of a stick or it may be tissue or cloth which is impregnated with the antiperspirant active material. 25

Test Method for Assessment of Efficacy of Antiperspirants

30 In the Examples given herein a test method is referred to for the assessment of the efficacy of an antiperspirant active agent. Details of the test procedure are described below. The test method for the assessment of antiperspirant efficacy depended on subjecting human volunteers to thermal stress and gravimetric determination of axillar sweat. 30

Test method

35	Subjects	A panel of up to 54 women who use no antiperspirant for the 14 days before the test.	35
40	Hot Room	Temperature 37°C ± 1°C, relative humidity approximately 35%.	40
	Test Product	10% solution of treated aluminium chlorhydrate (unless stated otherwise) in water.	
45	Control Product	10% solution of untreated aluminium chlorhydrate (unless stated otherwise) in water.	45
	Product Application	Approximately 0.5 g of solution was applied to each axilla with a pump-spray applicator.	
50	Sweat Collection	Absorbent cotton pads are used to collect the sweat. On entering the hot room each subject has a pair of pads placed in her axillae. After 40 minutes these are removed and rejected. Sweat is then collected for two consecutive periods of 20 minutes, fresh tared pads being used for each collection, and sweat weight determined.	50
55			55
60	Test Design	Subjects attend daily for 3 consecutive days. They receive one treatment with the products each day. On the third day the treatment is immediately followed by a hot room sitting and sweat collection.	60

Analysis of Data

The statistical treatment includes an analysis of variance which allows for subject, side and product effects. The efficacy is calculated from the geometric mean weight of sweat collected from the axillae treated with each product.

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$$\% \text{ reduction} = 100 \frac{C - T}{C}$$

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where C is the geometric mean sweat weight from the axillae treated with the control product and T is the geometric mean sweat weight from the axillae treated with the test product. The % reduction is usually calculated for each day separately and for the entire test.

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Significance is calculated by applying Student's T-test to the logarithmically transformed weights.

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Determination of Percentage Aluminium in Polymeric Species having a size greater than 100 Angstroms

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The percentage of water is given by

$$\frac{1,800 \times}{\text{Empirical weight of anhydrous } \text{Al}_2(\text{OH})_6\text{Cl}_a + 18x}$$

The following Examples illustrate the invention. Percentages are by weight.

Example 1

A solution was prepared from 50 g of aluminium chlorhydrate, having an Al/Cl ratio of 1.91 and a water content of 18.8%, and 8.9 g of glycine in 500 g of solution to give an Al/glycine ratio of 4. Samples of this solution were heated in 20 ml Pyrex glass screw cap tubes equipped with polytetrafluoroethylene washers to 120°C over 2 hours and maintained at this temperature for a further 3 hours; the word "Pyrex" is a trade mark. The resulting solution contained 20.2% of the aluminium as polymeric species exceeding 100 Angstroms in effective diameter. When tested for antiperspirancy by the method described herein, employing a panel of 22 subjects, this solution gave a 19% reduction in sweat collected compared to a 10% solution of untreated aluminium chlorhydrate as control. This result was significant at the 5% level.

Example 2

A batch of aluminium chlorhydrate having an Al/Cl molar ratio of 2.04 and a water content of 18.5% was dissolved in deionised water to give a 10% solution. Aliquots of this solution were taken, to which varying amounts of glycine were added, and the whole heated at 120°C for 3 hours. The percentage aluminium present as polymeric species with effective diameters in excess of 100 Angstroms is listed as a function of the amount of glycine present (per 100 g of solution).

	Wt glycine (g)	% Al in polymers > 100 Angstroms	Al:glycine molar ratio	
35	0	19.2		35
	0.75	21.1	10.00	
	1.87	22.5	4.00	
40	3.75	28.1	2.00	40
	5.62	31.7	1.33	
45	7.50	42.4	1.00	45

Example 3

Aluminium chlorhydrate (Al:Cl ratio 2.01) was made up as a 10% solution in deionised water. 100 g aliquots of this solution were taken and heated in 25 ml Pyrex screw cap tubes equipped with polytetrafluoroethylene washers, at 120°C, for times of 0, 1, 2, 3, 4 and 5 hours. To each 100 g of these heated solutions were added 3.75 g glycine and the samples then returned to the oven at 120°C for a further 6, 5, 4, 3, 2 and 1 hours, respectively, giving a total reaction time of 6 hours. The aluminium:glycine molar ratio of these solutions is 2. The percentage aluminium found as polymeric material with effective diameter in excess of 100 Angstroms is listed as a function of reaction conditions.

	Heating time with no glycine added (hours)	Heating time in the presence of glycine (hours)	% Al in polymers > 100 Angstroms	
5	0	6	63.8	5
	1	5	53.4	
10	2	4	55.0	10
	3	3	50.8	
	4	2	46.8	
15	5	1	49.5	15

Example 4

20 Solutions of aluminium chlorhydrate having an Al/Cl molar ratio of 2.00 were made up at concentrations between 10% and 40%. Each 100 g of these solutions contained 7.5 g glycine, with corresponding aluminium:glycine molar ratios varying between 1:1 to 4:1. The solutions were heated at 120°C for a period of 6 hours and the percentage aluminium found as polymeric species with effective diameters in excess of 100 Angstroms, determined. These results are tabulated along with data for reactions in which aluminium chlorhydrate is heated with no glycine present.

	% Aluminate Chlorhydrate	% Al in polymers > 100 Angstroms (no glycine present)	% Al in polymers > 100 Angstroms (glycine present) ^a	Al/glycine ratio in <i>a</i>	
30	10	28.8	78.1	1	30
	15	20.8	75.7	1.5	
35	25	none	26.9	2.5	35
	30	none	13.4	3.0	
40	40	none	4.1	4.0	40

Examples 5 to 8

45 A 50% w/w solution of aluminium chlorhydrate having an Al/Cl molar ratio of 2.00 was diluted with deionised water to give a 10% w/w solution. Aliquots of this solution were taken and quantities of various neutral amino acids were added. The resulting solutions were heated in 20 ml Pyrex glass tubes, equipped with screw caps and polytetrafluoroethylene washers, to 120°C over 30 minutes and maintained at this temperature for a further 3 hours. The percentage of aluminium present as polymeric species with effective diameters greater than 100 Angstroms is listed as a function of the type and amount of amino acid present.

Example	Amino Acid	Wt. of Amino Acid (g) per 50 g of Solution	Al:Amino Acid Molar Ratio	% Al in Polymers > 100 Angstroms
-	none	0	-	10.9
5	L-Lysine HCl	3.47	2.5	15.9
6	Glycine	1.43	2.5	23.5
7	DL-Valine	2.22	2.5	26.1
8	DL-Alanine	1.69	2.5	31.7

Examples 9 and 10

A 12.1% w/w solution of a basic aluminium bromide having an Al/Br molar ratio of 2.00 was prepared. Aliquots of this solution were taken and quantities of a neutral or basic amino acid were added. Pyrex glass tubes, equipped with screw caps and polytetrafluoroethylene washers, to 120°C over 30 minutes and maintained at this temperature for a further 3 hours. The percentage of aluminium present as polymeric species with effective diameters greater than 100 Angstroms is listed as a function of the type and amount of amino acid present.

Example	Amino Acid	Wt. of Amino Acid (g) per 50 g of Solution	Al:Amino Acid Molar Ratio	% Al in Polymers > 100 Angstroms
-	none	0	-	18.0
9	Glycine	1.43	2.5	40.7
10	L-Arginine	0.94	8.8	25.9

Example 11

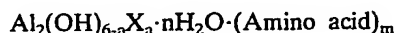
A solution was prepared from 9.34 g of 50% w/w aluminium chlorhydrate having an Al/Cl molar ratio of 2.00, 0.76 g of aluminium chloride hexahydrate and deionised water to give 50 g of a solution with an Al/Cl molar ratio of 1.50. An aliquot of this solution was taken and the amino acid added. The resulting solution was placed in a Pyrex glass tube equipped with a screw cap and polytetrafluoroethylene washer and heated to 120°C over 30 minutes and maintained at this temperature for 3 hours. The percentage of aluminium present as polymeric species with effective diameters in excess of 100 Angstroms is listed as a function of the amount of the amino acid present.

Example	Amino Acid	Wt. of Amino Acid (g) per 50 g of Solution	Al:Amino Acid Molar Ratio	% Al in Polymers > 100 Angstroms
-	none	0	-	0.0
11	L-Arginine	1.65	5.0	29.6

In copending application No. 17344/77 (Serial No. 1597497) there is described and claimed an antiperspirant active agent comprising an aqueous solution of a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1 which solution contains polymeric species of a size greater than 100 Angstroms and within which species there is contained 2 to 80% by weight of the total aluminium, and which solution also contains a neutral amino acid.

WHAT WE CLAIM IS:

1. A process of preparing an aqueous solution of an antiperspirant active compound comprising heating an aqueous solution of a mixture of a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of 6.5 to 1.3:1 and an amino acid, the concentration of the basic aluminium compound in such solution and the temperature and time of heating the solution being such that there is produced in the solution polymeric species having a size greater than 100 Angstroms, said species being produced in such amount that 2 to 80% by weight of the total aluminium is contained within such species.
2. A process as claimed in claim 1, wherein the amino acid contains 2 to 10 carbon atoms.
3. A process as claimed in claim 1 or claim 2, wherein the amino acid is a neutral amino acid.
4. A process as claimed in claim 3, wherein the amino acid is glycine, alanine, phenylalanine, valine, sarcosine, leucine or lysine hydrochloride.
5. A process as claimed in claim 1 or claim 2, wherein the amino acid is a basic amino acid.
6. A process as claimed in claim 5, wherein the amino acid is arginine, ornithine or lysine.
7. A process as claimed in any of the preceding claims, wherein the aluminium to amino acid molar ratio is from 20:1 to 1:1.
8. A process as claimed in any of the preceding claims, wherein the weight of the aluminium in the species having a size greater than 100 Angstroms is 5 to 60% of the total weight of the aluminium.
9. A process as claimed in any of the preceding claims, wherein the solution is heated at a temperature of from 80 to 140°C.
10. A process as claimed in any of the preceding claims, wherein the solution is heated for from 0.5 hour to 30 days.
11. A process as claimed in any of the preceding claims, wherein the basic aluminium compound is present in a concentration of from 5 to 60% by weight.
12. A process of preparing an antiperspirant active compound in solid form by drying the aqueous solution prepared according to the process claimed in any of the preceding claims to obtain an antiperspirant active complex having the empirical formula



- where X is Cl, Br, I or NO₃, *a* is from 0.3 to 1.5, *n* is from 0.5 to 8, and *m* is from 0.1 to 2.
13. An antiperspirant composition comprising an aqueous solution of an antiperspirant active compound prepared by the process claimed in any of claims 1 to 11 in combination with an adjunct which is a perfume, thickener, alcohol or propellant.
 14. An antiperspirant composition comprising a solid complex antiperspirant active agent prepared by the process claimed in claim 12 in combination with a powdered inert solid diluent or organic liquid carrier.
 15. A package consisting of the combination of an antiperspirant composition as claimed in claim 13 or claim 14 and an applicator for applying the antiperspirant composition to the skin.
 16. A process of preparing an aqueous solution of an antiperspirant active compound as claimed in claim 1 substantially as herein described with reference to any of Examples 1 to 11.
 17. An aqueous solution of an antiperspirant active compound prepared by a process as claimed in any of claims 1 to 11 or 16.

R.H. DOUCY,
Chartered Patent Agent.

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